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The Sequential Precipitation Titration of Arsenite and Arsenate with Silver Nitrate

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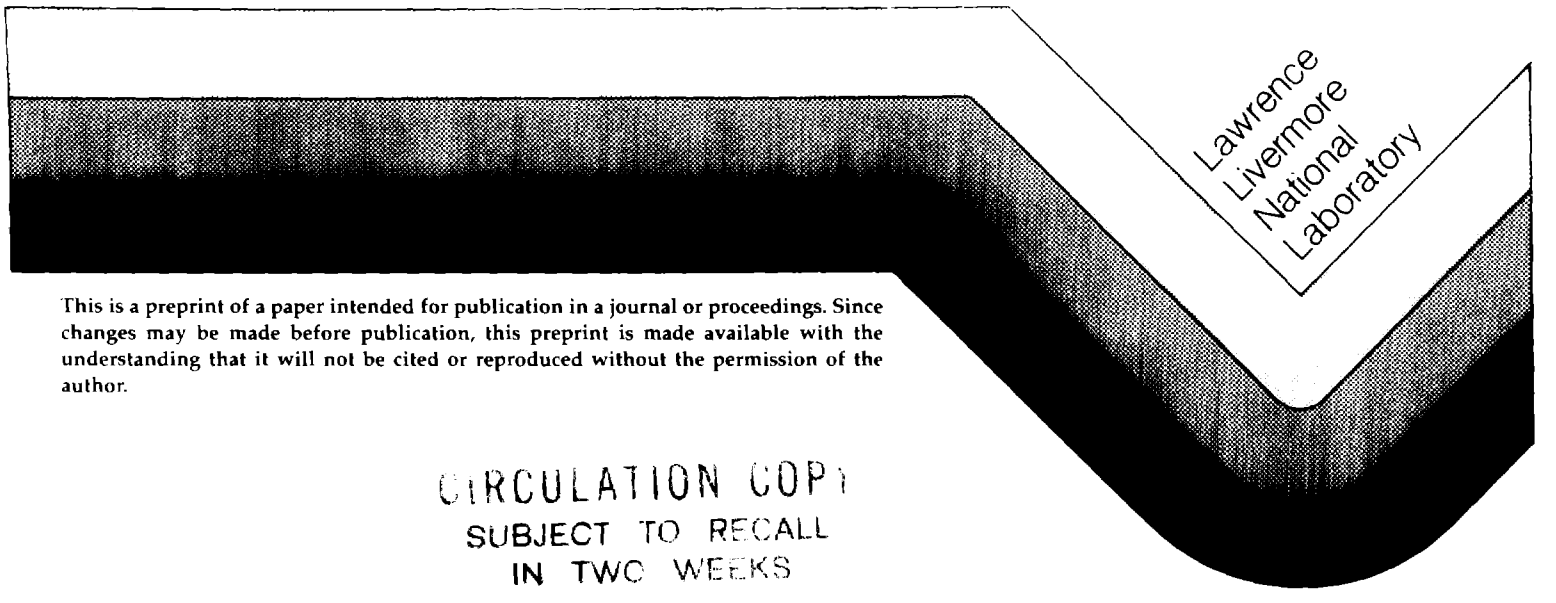

LETTER TO THE EDITOR

THE SEQUENTIAL PRECIPITATION TITRATION OF ARSENITE AND ARSENATE WITH SILVER NITRATE

Chao and Cheng (1) determined arsenite and arsenate by sequential titration with silver nitrate, using a silver/sulfide ion-selective indicator electrode. The method is practical because the solubility products of the precipitates differ by several orders of magnitude (-log K_{sp} at 20°C for Ag_3AsO_3, 31.27 and for Ag_3AsO_4, 22.19). These authors checked and continually adjusted the pH to 11.0 with dilute sodium hydroxide or nitric acid. In the same paper the authors state that, for the titration of arsenite, a buffer is needed and recommend a sodium hydroxide solution containing some carbonate.

Masson (2) determined arsenate by a similar method using a borate buffer. We have found this buffer (a 0.025 M solution of sodium tetraborate decahydrate) suitable for the sequential microdetermination of arsenite and arsenate and consider the method simpler than the method involving pH adjustment used by Chao and Cheng (1). Arsenite yields a steep titration curve with silver nitrate in aqueous solution. Arsenate, however, because of the larger solubility of its silver salt, yields much shallower titration curves which are enhanced by a partially nonaqueous medium such as 50% methanol. When both anions coexist in solution, the arsenite break is greatly suppressed in 50% methanol. In 25% methanol somewhat better titration curves are obtained for arsenite, but its recovery is not as good as in aqueous

solution, as shown in Table 1. We have at present no explanation for the suppression of the arsenite break in the presence of arsenate in partially nonaqueous media.

A typical titration curve for 0.9 mg of arsenic as arsenite and of 0.6 mg of arsenic as arsenate is shown in Figure 1. Recalculation of the data of Chao and Cheng (1) showed that for arsenite their recoveries varied from -1.02 to +6.1% of the nominal, while for arsenate they varied from -0.9 to +7.6%. This is consistent with our results.

In summary, microamounts of arsenite and arsenate can be determined in borate-buffered aqueous solution by potentiotitrimetry with silver nitrate.

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2. Masson, M.R., Microdetermination of selenium, tellurium, and arsenic in organic compounds. Mikrochim. Acta 1, 399-411 (1976).

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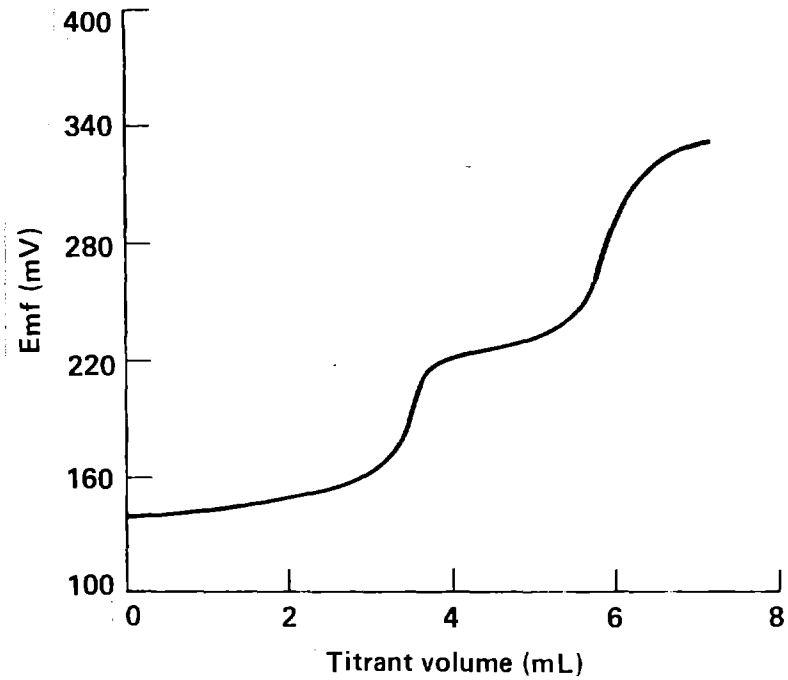

Figure 1. Titration curve for 0.9 mg of As as arsenite and 0.6 mg of As as arsenate (in sequence) in aqueous solution.

TABLE 1

Recovery of Arsenite and Arsenate by Titration with 0.01 N Silver Nitrate

Taken (mmol)		Medium	Mean recovery, percent (standard deviation)		
Arsenite	Arsenate		Arsenite	Arsenate	No. replicates
0.0122	0.008	Aqueous	100.5 (0.67)	98.3 (0.98)	4
0.0122	0.008	25% methanol	103.7 (0.51)	93.5 (1.10)	4